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(54) Silica reinforced rubber composition and use in tires

(57) The invention relates to the preparation of a composite of an elastomer composition containing silica-based reinforcement created by a controlled alkoxy silane condensation reaction within the elastomer matrix. The invention also relates to such composite and to a tire having at least one component of such composite.

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Description**Field**

5 [0001] The invention relates to the preparation of a composite of an elastomer composition containing silica-based reinforcement created by a controlled alkoxysilane condensation reaction within the elastomer matrix. The Invention also relates to such composite and to a tire having at least one component of such composite.

Background

10 [0002] Elastomer compositions typically contain particulate filler reinforcement such as, for example, carbon black and/or silica.

[0003] Silica reinforcement for an elastomer composition may be provided by adding particulate silica such as, for example, precipitated silica, to a rubber composition.

15 [0004] Alternatively, silica reinforcement may be formed in-situ within an elastomer host by a condensation of an alkoxysilane to form, for example, a polysiloxane within the elastomer matrix.

[0005] It is a purpose of this invention to enhance such a formation of the alkoxysilane condensation reaction product within an elastomer host.

20 [0006] While it is known that various condensation reactions may be promoted or retarded by the presence of acidic or base materials, such phenomenon as applied to an alkoxysilane, particularly an alkoxysilane polysulfide, condensation within an elastomer host is believed to be novel and inventive.

[0007] In practice, particularly where a particulate silica-based filler is added to an elastomer composition as an elastomer reinforcement such as, for example, an aluminosilicate or silica-modified carbon black, a coupling agent is often used to aid in coupling the filler to one or more diene-based elastomers. The use of various coupling agents for 25 such purpose is well known to those having skill in such art.

30 [0008] Such coupling agents may be, for example, an alkoxyorganosilane polysulfide which has a constituent component, or moiety, (the alkoxysilane portion) capable of reacting with, for example, silanol groups, on the silica surface of the silica-containing filler and, also, a constituent component, or moiety, (the polysulfide portion) usually capable of interacting with the rubber, particularly a diene-based, sulfur vulcanizable rubber which contains carbon-to-carbon double bonds, or unsaturation. In this manner, then, the coupler may act as a connecting bridge between the silica-containing filler and the rubber and, thereby, enhance its reinforcing effect for the rubber composition.

35 [0009] In particular, it is envisioned that the silane moiety of the coupler, particularly a trialkoxysilane moiety, is available for reacting with virtually any reactive hydroxyl groups it may encounter and particularly with silanol groups (-Si-OH) on the surface of the silica-based filler and also with alkoxy groups on the coupler itself to form siloxane units (-Si-O-Si-).

[0010] In practice, alkoxyorganosilane polysulfides sometimes used are bis-(3-trialkoxysilylalkyl) polysulfides which contain from 2 to 8, with an average of from 3.5 to 4.5, sulfur atoms in its polysulfidic bridge.

[0011] During a typical mixing (processing) of the elastomer composition in an internal rubber mixer under high shear conditions to temperatures in a range of 150°C to 175°C, the silane portion reacts with the surface of a silica-based filler (e.g.: which may be hydroxyl groups on the surface of the silica which may be in a form of silanol groups).

40 [0012] A portion of the polysulfidic bridge of such organosilane polysulfide typically breaks during such mixing operation, resulting in an exposed sulfur on the coupling agent which is available to apparently interact with one or more of the elastomer(s) in the elastomer composition.

[0013] However, it is to be appreciated that such interaction of the sulfur with the elastomer(s) is typically accompanied by an increase in the viscosity (e.g.: Mooney viscosity) of the rubber composition itself as the sulfur interacts with the elastomer(s). Too high of an elastomer viscosity under such conditions makes the rubber composition more difficult to process, or mix, in a typical internal rubber mixer.

45 [0014] Therefore, a degree of adjustment of various formulation ingredients (formulation tuning) and enhancement of various physical properties is limited because of such typical higher viscosity related processing limitations imposed 50 via use of such coupling agent.

[0015] Uniquely, however, organosilane polysulfide compounds in a form of organosilane disulfide compounds with predominately contained only two sulfur atoms in the polysulfidic bridge (e.g. and an average of 2 to 2.6 sulfur atoms) do not ordinarily cause such excessive viscosity build-up of the rubber composition during its internal mixing operation.

55 [0016] Such phenomenon in the use of the organosilane disulfide compounds is apparently due to stronger sulfur-to-sulfur bonds for the polysulfidic bridge of the disulfide and their inherent resistance to breaking upon high shear mixing at the aforesaid elevated temperatures, thus, enabling only a very limited amount of sulfur atoms available to interact with diene-based elastomer(s) in the rubber composition during the mixing operation. This phenomenon is well known to those having skill in such art.

[0017] Accordingly, it is desired to more effectively utilize the aforesaid rubber processing advantages afforded via use of such organosilane disulfide compound, including a bis-(trialkoxyorganosilane) disulfide, compound as a coupling agent.

[0018] The term "phr" as used here, and according to conventional practice, refers to "parts of a respective material per 100 parts by weight of rubber, or elastomer".

[0019] In the description of this Invention, the terms "rubber" and "elastomer" if used herein, may be used Interchangeably, unless otherwise prescribed. The terms such as "rubber composition", "compounded rubber" and "rubber compound", if used herein, are used interchangeably to refer to "rubber which has been blended or mixed with various ingredients and materials" and "rubber compounding" or "compounding" may be used to refer to "the mixing of such materials". Such terms are well known to those having skill in the rubber mixing or rubber compounding art.

Summary and Practice of the Invention

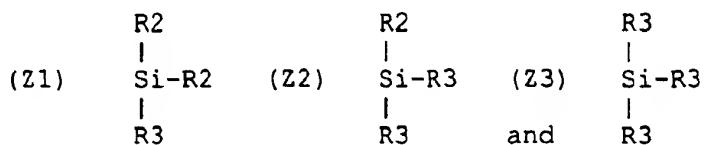
[0020] - In accordance with this invention, a process of preparing a composite of an elastomer composition which contains a silica-based reinforcement therein comprises the sequential steps of:

(A) thermomechanically mixing in at least one preparatory mixing step to a temperature of 140°C to 190°C, alternatively to 150°C to 185°C, (i) 100 parts by weight of at least one sulfur vulcanizable elastomer selected from homopolymers and copolymers of conjugated diene hydrocarbons copolymers of at least one conjugated diene hydrocarbon and vinyl aromatic compound, (ii) 15 to 100, alternatively 30 to 90, phr of particulate filler comprised of at least one silica-based filler which contains reactive hydroxyl groups on the surface thereof (e.g.: silanol groups), (iii) 0.05 to 20 parts by weight per part by weight of said particulate filler of at least one organosilane compound, preferably a polysulfide compound and, more preferably, a disulfide selected from at least one of Formula (I) and (II) their mixtures:



30 wherein n is an integer of from 2 to 8 with an average of from 3.5 to 4.5, or an integer of from 2 to 4 with an average of from 2 to 2.6;

wherein Z is selected from the group consisting of:



wherein Z is preferably (73):

45 wherein Z is preferably (20),
wherein R_1 is selected from the group consisting of a substituted or unsubstituted alkylene group having a total of 1 to 18 carbon atoms and a substituted or unsubstituted arylene group having a total of 6 to 12 carbon atoms, preferably alkylenes having from 2 to 6 carbon atoms; wherein R_2 may be the same or different and is individually selected from the group consisting of alkyls having 1 to 4 carbons and phenyl; and R_3 may be the same or different and is individually selected from the group consisting of alkoxy groups having 1 to 4 carbon atoms, preferably from 1 to 2 carbon atoms; and

50 wherein X is selected from mercapto, thiocyanato, amino, vinyl, epoxide, acrylate and methacrylate groups, preferably mercapto, epoxide and amine groups; (iv) subsequently mixing therewith at least one silane condensation reaction promoter and/or inhibitor.

(B) subsequently blending sulfur therewith, in a final thermomechanical mixing step at a temperature to 100°C to 130°C.

55 [0021] For said final mixing step, usually elemental sulfur is added in an amount of 0.4 to 3 phr.
[0022] In practice, the silica-based fillers are preferably selected from at least one of precipitated silica, aluminosil-

[0023] In one aspect of the Invention such process is provided wherein said preparatory mixing is conducted in at least two sequential thermomechanical mixing steps in at least one internal rubber mixer; wherein at least two of said mixing steps are conducted at a temperature in a range of 140°C to 190°C, with intermediate cooling of the rubber composition between at least two of said mixing steps to a temperature below 50°C.

5 [0024] In practice, the total, cumulative period of mixing, namely period of mixing in an internal rubber mixer(s), for the said preparatory mixing step(s) (A) is in a range of 3 to 20, alternatively 5 to 15, minutes.

[0025] In practice, the period of mixing for the final thermomechanical mixing step, namely period of mixing in an internal rubber mixer, (B) is in a range of from one to five minutes.

[0026] In further accordance with process of this Invention, said preparatory mixing step (A) is composed of at least 10 two sequential mixing stages in which said elastomer, said particulate silica-based filler and said organosilane polysulfide compound, preferably an organosilane disulfide compound, are added and mixed in one or more sequential mixing stages and in which said silane condensation reaction promoter or inhibitor is added subsequently to the addition of both of said particulate filler and organosilane polysulfide in the same or subsequent mixing stage.

15 [0027] In additional accordance with the process of this invention, said preparatory step (A) is composed of at least two sequential mixing stages in which 20 to 60 weight percent of each of the said silica-based filler, and said organosilane polysulfide compound, preferably an organosilane disulfide compound, are added and mixed in a first preparatory mixing stage and the remainder thereof added and mixed in at least one subsequent preparatory mix stage and the silane condensation promoter or inhibitor added and mixed subsequent to the completed addition of said filler and organosilane polysulfide in the same or subsequent mixing stage.

20 [0028] In practice, the organosilane polysulfide compound, preferably said organosilane disulfide compound, is optionally added to the thermomechanical preparatory mixing step in a form of a particulate comprised of (a) 25 to 75, preferably 40 to 60, weight percent of said organosilane polysulfide compound and, correspondingly, (b) 75 to 25, preferably 60 to 40, weight percent carbon black. A purpose of providing the organosilane polysulfide compound in a form of a particulate in the process of this invention is to add the organosilane polysulfide in a form of a relatively dry, or substantially dry, powder in which the carbon black acts as a carrier for the organosilane polysulfide in the process of this invention, particularly where the organosilane polysulfide would normally otherwise be in a liquid, or substantially liquid, form. A contemplated benefit for the particulate is to aid in the dispersing of the organosilane polysulfide in the preparatory mixing step(s) of the process of this invention and to aid in the introduction of the organosilane polysulfide into the preparatory mixing of the rubber composition mixture.

25 [0029] In further accordance with this invention, a rubber composition is provided which is prepared by the process of this invention.

[0030] In additional accordance with the Invention, the process comprises a subsequent step of sulfur vulcanizing the prepared rubber composition, preferably at a temperature in a range of 140°C to 190°C.

30 [0031] Accordingly, the invention also thereby contemplates a sulfur-vulcanized rubber composition, prepared by the process of the invention.

[0032] In additional accordance with the invention, the process comprises the additional, subsequent steps of preparing an assembly of a sulfur-vulcanizable rubber composition having at least one component of an unvulcanized (or vulcanized) rubber composition prepared by the process of this invention and vulcanizing the assembly at a temperature in a range of 140°C to 190°C.

35 [0033] In one aspect of the Invention, such assembly is a tire and, preferably, such component is a tire tread.

[0034] Accordingly, the invention also comprises a vulcanized tire prepared by such process.

[0035] Also, accordingly, the invention comprises said tire wherein the said component is a tread.

[0036] In a further aspect of the Invention, optionally a total of 0.05 to 5 phr of at least one alkoxy silane, preferably an alkyl alkoxy silane, can be thermomechanically mixed in said preparatory mixing stage(s), particularly where said 40 alkoxy silane has the formula: R'-Si-(OR)₃, where R is a methyl, ethyl, propyl or isopropyl radical, preferably a methyl and/or an ethyl radical and R' is a saturated alkyl radical having from 1 to 18, alternatively from 2 to 6, carbon atoms, or an aryl or saturated alkyl substituted aryl radical having from 6 to 12 carbon atoms. Such aryl or substituted aryl radicals might be, for example, benzyl, phenyl, tolyl, methyl tolyl, and alpha-methyl tolyl radicals. Preferably, R is an alkyl radical.

45 [0037] A purpose of the alkoxy silane is, for example, to improve filler incorporation and compound aging. Representative examples of alkyl alkoxy silanes are, for example but not intended to be limited to, propyltriethoxysilane, methyltriethoxysilane, hexadecyltriethoxysilane, and octadecyltriethoxysilane.

50 [0038] For an additional aspect of this Invention, optionally from 5 to 40 phr of a starch composite of starch and plasticizer may be thermomechanically mixed in said preparatory mixing stage(s).

[0039] Such starch composite preferably has a softening point in a range of 110°C to 160°C according to ASTM No. 55 D1228.

[0040] Starch conventionally has a softening point in a range of 180°C to 220°C which is above normal rubber compound mixing temperatures. Accordingly, a starch/plasticizer combination, or as a composite thereof, is used with the plasticizer component having a melting point below 180°C such as, for example, poly(ethylene vinyl acetate), cellulose

acetate and diesters of dibasic organic acids, so long as they have a softening point below 180°C and preferably below 160°C. It is contemplated that such starch composites contain hydroxyl groups on the surface thereof which are available for reaction with coupling agents as described below. Representative examples of use of starch composites in rubber compositions may be found, for example, in US-A-5,672,639.

5 [0041] A significant feature of this invention is the utilization of a silane condensation reaction promoter and/or inhibitor to control the rate of in-situ formation, a polysiloxane network which is accomplished by the condensation of the silane coupling agent within the rubber composition.

10 [0042] Accordingly, the silane condensation reaction may be facilitated, for example, by a promoter where it is desired to increase the condensation reaction rate or by a condensation reaction inhibitor where it is desired to retard the condensation reaction rate.

15 [0043] While the mechanism may not be completely understood, it is hypothesized that a polysiloxane-based network (e.g.: a network of at least partially entangled polysiloxane polymer chains) is created by an in-situ formation of a polysiloxane-based polymer chain, resulting from silane condensation, extending into and within already formed polymer chains of the elastomer host. This phenomenon can take place at the interface (filler/elastomer) which means at the vicinity of the filler surface and/or in the polymer matrix.

20 [0044] For example, it is hypothesized that utilization of a bis-(trialkoxyorganosilane) polysulfide compound, preferably a bis-(trialkoxyorganosilane) disulfide compound, in combination with a silane condensation reaction promoter for enhancing a reaction of the bis-(trialkoxyorganosilane) polysulfide compound with silanol groups on the silica-based filler and, also, alkoxy moieties of the trialkoxyorganosilane polysulfide compound, react to form a polysiloxane which in turn, may lead to formation of a polysiloxane network at the surface of the filler and/or within the elastomer.

25 [0045] For another significant aspect of the practice of the invention, it is considered herein that a significant departure from past practice, when using a bis-(alkoxyorganosilane) disulfide compound which contains an average of from 2 to 2.6 sulfur atoms in its polysulfidic bridge is (1) promoting a creation of the polysiloxane polymer network via the required promotion of the alkoxy silane condensation reaction which would be accompanied by an expected increase in viscosity of the overall elastomer composition with, correspondingly, a somewhat adverse impact upon its processability because of the increase in rubber composite viscosity yet, however, (2) in the absence of viscosity-increasing sulfur moieties being liberated because the bis-(alkoxyorganosilane) polysulfide compound is a disulfide compound containing the aforesaid average of only 2 to 2.6, instead of the aforesaid 3.5 to 4.5, connecting sulfur atoms in its polysulfide bridge.

30 [0046] Indeed, it is the very use of a bis(alkoxyorganosilane) disulfide compound with the aforesaid sulfur units of the polysulfide bridge being limited to an average of 2 to 2.6, instead of using a bis-(alkoxyorganosilane) polysulfide with an average of 3.5 to 4.5 sulfur atoms in its polysulfidic bridge that enables an operational freedom in processing the unvulcanized rubber composition to be able to tolerate an increase in viscosity of the rubber composition via promoting the aforesaid silane condensation reaction.

35 [0047] As a result, a new method has been discovered to modify, or tune, various physical properties of elastomers via use of chemical control in addition to the thermomechanical mixing conditions.

[0048] In the practice of this invention, various acidic or basic condensation promoters may be used and, in general, are understood to be well known to those having skill in such art.

40 [0049] For example, representative of basic promoters are, for example, ammonia, ammonium hydroxide, n-butylamine, terbutylamine, tetrahydrofuran (THF), sodium fluoride, various polyamines such as, for example, pentaethylene hexamine, diaminopropane, diethylenetriamine, triethylenetetramine and polyallylamines such as, for example, poly(allylaminehydrochloride), poly(L-lysine hydrobromide), poly(L-arginine hydrochloride) and poly(L-histidine hydrochloride).

45 [0050] Usually, preferred basic condensation reaction promoters may be amines such as, for example, n-butylamine, or polyamines such as, for example, pentaethylenehexamine and polyallylamines such as, for example, poly(L-lysine hydrobromide, where a basic condensation reaction promoter is desired.

[0051] For example, representative of acidic condensation reaction promoters are phosphoric acid, acetic acid, hydrofluoric acid and sulfuric acid; wherein acetic acid and sulfuric acid are usually preferred where an acidic condensation reaction promoter is desired.

50 [0052] Metal salts and metal oxides can also be used as promoters or inhibitors of silane condensation reactions (i.e.: Lewis acid or base reactions).

[0053] Representative examples of metal salts are, for example, zinc sulfate, aluminate sulfate, zinc stearate, and aluminum stearate, wherein aluminum stearate may be preferred where a metal salt condensation reaction promoter is desired.

55 [0054] Representative examples of metal oxides are, for example, zinc oxide and aluminum oxide, wherein zinc oxide may be preferred where a metal oxide condensation reaction inhibitor is desired.

[0055] Typical catalysts for condensation reaction curing of silicon rubber might also be used. Examples are metal carboxylates such as, for example, bis(2-ethylhexanoate) tin, bis(neodecanoate) tin, and dibutyl tin diacetate, as well as

dibutyl tin dilaurate, stannous octoate, stannous acetate, lead naphthanate, cobalt naphthanate and zinc octoate, wherein dibutyl tin dilaurate and cobalt naphthanate may be preferred where a catalyst is desired for use in a silane condensation reaction.

[0056] The actual selection of condensation promoter will depend somewhat upon the sensitivity of the rubber matrix, or composition, itself and the balance of desired physical properties. Such selection can readily be made by one having skill in such art.

[0057] Thus, the condensation reaction may be controlled by an acid or a basic promoter, depending somewhat upon the magnitude of the effect desired and the silica-based filler used. For example, for silica which is acidic in nature, a base type of silane condensation would be expected to be used. For a carbon black type of filler which is basic in nature, an acid type of silane condensation reaction promoter would be expected to be used followed with a basic type of silane condensation reaction promoter. It is believed that such use acid/base type of condensation reaction promoters is well known to one having skill in such art.

[0058] Thus, for example, while individual circumstances may vary, an acid or base condensation reaction promoter, or any other suitable condensation reaction promoter, may be added to promote, first, the alkoxy silane hydrolysis (acidic promoter) and then, secondly, the silane condensation reaction (basic promoter) leading to a formation of a condensed polysiloxane polymer network within the host elastomer composition.

[0059] A typical characteristic of an acid-oriented type of promoter is its possible coordination on the oxygen of the alkoxy group to promote its departure and silane hydrolysis which, in turn, promotes the silane condensation reaction.

[0060] A typical characteristic of a base-oriented type of promoter is its possible coordination on the silicon atom of an alkoxyorganosilane to promote a departure of one or more of the alkoxy groups and therefor favors condensation reactions.

[0061] Also, either of the acid-oriented type or base-oriented type of promoter may act to disturb the H⁺-OH-equilibrium at the filler surface thereby indirectly affecting silane condensation also catalyzed by H⁺-OH⁻. Such phenomena is understood to be well known to those having skill in such art.

[0062] According to this invention, a bis-(alkoxyorganosilane) polysulfide, preferably a relatively high purity disulfide material version which does not appreciably release free sulfur under the prescribed conditions, is used in addition to a silane condensation promoter.

[0063] While the mechanism might not be completely understood, it is contemplated that a combination of the bis-(alkoxyorganosilane) polysulfide, preferably a disulfide, compound and condensation promoter or inhibitor (retarder) acts to chemically tune, or control, the silane reactivity, assist in the formation of polysiloxane polymer network within the elastomer host with a result of modifying both the processing of the rubber composition and, also, resultant physical properties of the rubber composition.

[0064] Where it is desired for the rubber composition, which contains both a siliceous filler such as silica, alumina and/or aluminosilicates, carbon black and silica-modified carbon black reinforcing pigments, to be primarily reinforced with silica-based filler(s) as the reinforcing filler, it is often preferable that the weight ratio of such silica-based fillers to carbon black is at least 1/10 and preferably at least 10/1.

[0065] In one aspect of the invention, it is preferred that the silica-based filler is precipitated silica.

[0066] In another aspect of the invention, the filler is comprised of 15 to 95 weight percent precipitated silica, alumina, aluminosilicate and/or silica-modified carbon black, correspondingly, 5 to 85 weight percent carbon black; wherein the said carbon black has a CTAB value in a range of 80 to 150.

[0067] In a practice of this invention, said filler can be comprised of 60 to 95 weight percent of said silica, alumina, aluminosilicate and/or silica-modified carbon black, and, correspondingly, 40 to 5 weight percent carbon black.

[0068] The aluminosilicate can be prepared, for example, by co-precipitation of a sodium silicate and an aluminate. The preparation of aluminosilicates is well known to those having skill in such art.

[0069] The silica-modified carbon black may be prepared, for example, by reacting carbon black with a siloxane or by co-fuming carbon black and silica at an elevated temperature. Such methods of modifying carbon black with silica are known to those having skill in such art.

[0070] Representative examples of bis-(alkoxyorganosilane) disulfides of the aforesaid bis-(alkoxyorganosilane) polysulfide compound of Formula (I) include, for example: 2,2'-bis(trimethoxysilyl ethyl) disulfide; 3,3'-bis(trimethoxysilyl propyl) disulfide; 3,3'-bis(triethoxysilyl propyl) disulfide; 2,2'-bis(triethoxysilyl ethyl) disulfide; 3,3'-bis(triethoxysilyl propyl) disulfide; 2,2'-bis(triethoxysilyl ethyl) disulfide; 2,2'-bis(tri-sec. butoxysilyl ethyl) disulfide; 3,3'-bis(tri-t-butoxysilyl ethyl) disulfide; 3,3'-bis(triethoxysilyl tolylene) disulfide; 3,3'-bis(trimethoxysilyl tolylene) disulfide; 3,3'-bis(triisopropoxysilyl propyl) disulfide; 3,3'-bis(triethoxysilyl propyl) disulfide; 2,2'-bis(2-ethylhexoxysilyl ethyl) disulfide; 2,2'-bis(dimethoxy ethoxysilyl ethyl) disulfide; 3,3'-bis(methoxyethoxypropoxysilyl propyl) disulfide; 3,3'-bis(methoxy dimethylsilyl propyl) disulfide; 3,3'-bis(cyclohexoxy dimethylsilyl propyl) disulfide; 4,4'-bis(trimethoxysilyl butyl) disulfide; 3,3'-bis(trimethoxysilyl-3-methylpropyl) disulfide; 3,3'-bis(triethoxysilyl-3-methylpropyl) disulfide; 3,3'-bis(dimethoxy methylsilyl-3-ethylpropyl) disulfide; 3,3'-bis(trimethoxysilyl-2-methylpropyl) disulfide; 3,3'-bis(dimethoxy phanylsilyl-2-methylpropyl) disulfide; 3,3'-bis(trimethoxysilylcyclohexyl) disulfide; 12,12'-bis(trimethoxysilyldodecyl)

disulfide; 12,12'-bis (triethoxysilyldodecyl) disulfide; 18,18'-bis (trimethoxysilyloctadecyl) disulfide; 18,18'-bis (methoxydimethylsilyloctadecyl) disulfide; 2,2'-bis (trimethoxysilyl-2-methylethyl) disulfide; 2,2'-bis (triethoxysilyl-2-methylethyl) disulfide; 2,2'-bis (tripropoxysilyl-2-methylethyl) disulfide; and 2,2'-bis(trioctoxysilyl-2-methylethyl) disulfide.

[0071] Representative examples of compounds according to Formula (II) are, for example, mercapto propyl triethoxysilane, gamma-amino propyl triethoxysilane, vinyl triethoxysilane, gamma-glycidoxy propyltriethoxy silane, gamma-methacryloxypropyltriethoxysilane.

[0072] In general, preferred compounds according to Formula (II) are mercaptopropyltriethoxysilane, gamma-glycidoxy propyltriethoxysilane, gamma-aminopropyltriethoxysilane.

[0073] In the practice of this invention, as hereinbefore pointed out, the rubber composition is comprised of at least one diene-based elastomer, or rubber. Suitable conjugated dienes are isoprene and 1,3-butadiene and suitable vinyl aromatic compounds are styrene and alpha-methylstyrene. Thus, it is considered that the elastomer is a sulfur-curable elastomer. Such diene-based elastomer, or rubber, may be selected, for example, from at least one of cis 1,4-polyisoprene rubber (natural and/or synthetic), and preferably natural rubber), emulsion polymerization prepared styrene/butadiene copolymer rubber, organic solution polymerization prepared styrene/butadiene rubber, 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubbers, cis 1,4-polybutadiene, high vinyl polybutadiene rubber (35-90 percent vinyl), styrene/isoprene copolymers, emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer rubber and butadiene/acrylonitrile copolymer rubber.

[0074] By emulsion polymerization prepared E-SBR, it is meant that styrene and 1,3-butadiene are copolymerized as an aqueous emulsion. Such are well known to those skilled in such art. The bound styrene content can vary, for example, from 5 to 55%. In one aspect, the E-SBR may also contain acrylonitrile to form a terpolymer rubber, as E-SNBR, in amounts, for example, of 2 to 30 weight percent bound acrylonitrile in the terpolymer.

[0075] The solution polymerization prepared SBR (S-SBR) typically has a bound styrene content in a range of 5 to 55, preferably 9 to 36, percent. The S-SBR can be conveniently prepared, for example, by organo lithium catalyzation in the presence of an organic hydrocarbon solvent.

[0076] The 3,4-polyisoprene rubber (3,4-PI) is considered beneficial for a purpose of enhancing the tire's traction when it is used in a tire tread composition. When used, it is usually used in a minor amount of the rubber component(s) of a rubber composition (e.g.: 5 to 15 phr).

[0077] The 3,4-polyisoprene elastomer and use thereof is more fully described in US-A-5,087,668.

[0078] The cis 1,4-polybutadiene rubber is considered to be beneficial for a purpose of enhancing the tire tread's wear, or treadwear.

[0079] Such polybutadiene elastomer can be prepared, for example, by organic solution polymerization of 1,3-butadiene as is well known to those having skill in such art.

[0080] The cis 1,4-polybutadiene elastomer may be conveniently characterized, for example, by having at least a 90% cis 1,4-content.

[0081] The cis 1,4-polyisoprene and cis 1,4-polyisoprene natural rubber are well known to those having skill in the rubber art.

[0082] In the practice of this invention, it is further contemplated that alkoxy silane-terminated and tin coupled solution polymerization prepared elastomers may also be used.

[0083] The alkoxy silane-terminated elastomers may be prepared, for example, by introduction of a chloro-alkoxysilane, chloro-alkylalkoxysilane or 3,3'-bis-(triethoxysilylpropyl) disulfide, into the polymerization system during the preparation of the elastomer, usually at or near the end of the polymerization. Such termination of such elastomers and the preparation thereof are well known to those having skill in such art. Tin coupled elastomers are prepared by introducing a tin coupling agent during the polymerization reaction, usually at or near the end of the polymerization. Tin coupling of elastomers is well known to those having skill in such art.

[0084] Representative of tin coupled diene-based elastomers are, for example styrene/butadiene copolymers, isoprene/butadiene copolymers and styrene/isoprene/butadiene terpolymers.

[0085] In one aspect, it is preferred that a major portion, preferably at least 50 percent, and more generally in a range of 60 to 85 percent of the Sn bonds in the tin coupled elastomer, are bonded to diene units of the styrene/diene copolymer, or diene/diene copolymer as the case may be, which might be referred to herein as "Sn-dienyl bonds" (or Si-dienyl bonds), such as, for example, butadienyl bonds in the case of butadiene being terminus with the tin.

[0086] Creation of tin-dienyl bonds can be accomplished in a number of ways such as, for example, sequential addition of butadiene to the copolymerization system or use of modifiers to alter the styrene and/or butadiene and/or isoprene reactivity ratios for the copolymerization. It is believed that such techniques, whether used with a batch or continuous copolymerization system, is well known to those having skill in such art.

[0087] The tin coupling of the elastomer can be accomplished by relatively conventional means and is believed to be well known to those skilled in such art.

[0088] Various tin compounds can be used for such purpose and tin tetrachloride is usually preferred.

[0089] The tin coupled copolymer elastomer can also be tin coupled with an organo tin compound such as, for

example, alkyl tin trichloride, diethyl tin dichloride and trialkyl tin monochloride, yielding variants of a tin coupled copolymer with the trialkyl tin monochloride yielding simply a tin terminated copolymer.

[0090] Examples of tin modified, or coupled, styrene/butadiene might be found in, for example, US-A-5,064,910.

5 [0091] The vulcanized rubber composition should contain a sufficient amount of silica, and carbon black if used, reinforcing filler(s) to contribute a reasonably high modulus and high resistance to tear. The combined weight of the silica, alumina, aluminosilicates and/or silica-modified carbon black, as well as carbon black, as hereinbefore referenced, may be as low as 30 parts per 100 parts rubber, but is more preferably from 35 to 90 parts by weight.

[0092] While it is considered herein that commonly-employed siliceous pigments used in rubber compounding applications might be used as the silica in this invention, including pyrogenic and precipitated siliceous pigments (silica) 10 alumina, aluminosilicates, precipitated silicas are preferred.

[0093] The siliceous pigments preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate. Such precipitated silicas are well known to those having skill in such art.

15 [0094] Such precipitated silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of 40 to 600, and more usually in a range of 50 to 300 square meters per gram. The BET method of measuring surface area is described in the *Journal of the American Chemical Society*, Volume 60, page 304 (1930).

[0095] The silica may also be typically characterized by having a dibutylphthalate (DBP) value in a range of 100 to 350, and more usually 150 to 300 cm³/100g (ASTM D2414).

20 [0096] Further, the silica, as well as the aforesaid alumina and aluminosilicate may be expected to have a CTAB surface area in a range of 100 to 220 m²/g (ASTM D3849). The CTAB surface area is the external surface area as evaluated by cetyl trimethylammonium bromide with a pH of 9. The method is described in ASTM D 3849 for set up and evaluation. The CTAB surface area is a well known means for characterization of silica.

25 [0097] Mercury surface area/porosity is the specific surface area determined by Mercury porosimetry. For such technique, mercury is penetrated into the pores of the sample after a thermal treatment to remove volatiles. Set up conditions may be suitably described as using a 100 mg sample; removing volatiles during 2 hours at 105°C and ambient atmospheric pressure; ambient to 2000 bars pressure measuring range. Such evaluation may be performed according to the method described in Winslow, Shapiro in ASTM bulletin, p.39 (1959) or according to DIN 66193. For such an evaluation, a CARLO-ERBA Porosimeter 2000 might be used.

30 [0098] The average mercury porosity specific surface area for the silica should be in a range of 100 to 300 m²/g.

[0099] A suitable pore size distribution for the silica, alumina and aluminosilicate according to such mercury porosity evaluation, is considered herein to be:

35 five percent or less of its pores have a diameter of less than 10 nm; 60 to 90 percent of its pores have a diameter of 10 to 100 nm; 10 to 30 percent of its pores have a diameter of 100 to 1000 nm; and 5 to 20 percent of its pores have a diameter of greater than 1000 nm.

[0100] The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly 40 larger, in size.

[0101] Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations Hi-Sil 210, 243, etc; silicas available from Rhone-Poulenc with, for example, designation of Zeosil 1165MP, silicas available from Degussa AG with, for example, designations VN2 and VN3, Ultrasil 7000GR, etc and silicas commercially available from Huber having, for example, a designation of Hubersil 8745.

45 [0102] Representative examples of alumina for the purposes of this invention are natural and synthetic aluminum oxide (Al₂O₃). Such alumina can be suitably, synthetically prepared, for example, by controlled precipitation of aluminum hydroxide. For example, neutral, acidic, and basic Al₂O₃ can be obtained from the Aldrich Chemical Company. In the practice of this invention, the neutral alumina is preferred, however, it is considered herein that the acidic, basic and neutral forms of alumina could be used. The neutral, or substantially neutral form is indicated as being preferential in order to use a form with reduced number of surface -OH groups as compared to the acidic form and, also, to reduce the basic sites of the alumina which are AlO-ions, representing a strong base, in order to reduce potential interferences with the desired reactions of the alumina with the organosilane disulfide coupler.

50 [0103] Representative examples of aluminosilicates for the purposes of this invention are, for example but not intended to be limited to, Sepiolite as a natural aluminosilicate which might be obtained as PANSIL from Tolsa S.A., Toledo, Spain and SILTEG as a synthetic aluminosilicate from Degussa AG. Such aluminosilicates can be used as natural materials or synthetically prepared, for example, as hereinbefore exemplified.

[0104] It is readily understood by those having skill in the art that the rubber composition would be compounded by

methods generally known in the rubber compounding art such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly-used additives such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur-vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts.

[0105] Typical amounts of reinforcing type carbon blacks(s), for this invention, if used, are hereinbefore set forth. It is to be appreciated that the silica coupler may be used in conjunction with a carbon black, namely, pre-mixed with a carbon black prior to addition to the rubber composition, and such carbon black is to be included in the aforesaid amount of carbon black for the rubber composition formulation. Typical amounts of tackifier resins, if used, comprise 0.5 to 10 phr, usually 1 to 5 phr. Typical amounts of processing aids comprise 1 to 50 phr. Such processing aids can include, for example, aromatic, naphthenic, and/or paraffinic processing oils. Typical amounts of antioxidants comprise 1 to 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others such as, for example, those disclosed in The Vanderbilt Rubber Handbook (1978), pages 344-346. Typical amounts of antiozonants comprise 1 to 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise 0.5 to 3 phr. Typical amounts of zinc oxide comprise 2 to 5 phr. Typical amounts of waxes comprise 1 to 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise 0.1 to 1 phr. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide.

[0106] The vulcanization is conducted in the presence of a sulfur-vulcanizing agent. Examples of suitable sulfur-vulcanizing agents include, for example, elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts which are conventionally added in the final, productive, rubber composition mixing step. Preferably, in most cases, the sulfur-vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur-vulcanizing agents are used, or added in the productive mixing stage, in an amount ranging from 0.4 to 3 phr, or even, in some circumstances, up to 8 phr, with a range of from 1.5 to 2.5, sometimes from 2 to 2.5, being usually preferred.

[0107] Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally and preferably, a primary accelerator(s) is used in total amounts ranging from 0.5 to 4, preferably 0.8 to 1.5, phr. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in smaller amounts (of 0.05 to 3 phr) in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators might be expected to produce a synergistic effect on the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

[0108] The rubber composition of this invention can be used for various purposes. For example, it can be used for various tire compounds. Such tires can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those having skill in such art.

[0109] The invention may be better understood by reference to the following examples in which the parts and percentages are by weight unless otherwise indicated.

45 EXAMPLE I

[0110] Sulfur-vulcanizable rubber compositions which contain silica reinforcement are prepared utilizing a relatively high purity bis(3-triethoxysilylpropyl) disulfide compound.

[0111] Such rubber compositions are identified herein as Samples A, B and C, with Sample A being considered herein as a Control sample.

[0112] For Samples B and C, a pentaethylenehexamine promoter is also added in the non-productive mixing stage after the silica-based filler and coupling agent have been added.

[0113] Rubber compositions containing the ingredients shown in Table 1 were prepared in a BR Banbury internal rubber mixer via the aforesaid sequential three separate stages of mixing, namely, two preparatory mix stages followed by a final mix stage to temperatures of 170°C, 170°C and 120°C and times of 8 minutes, 2 minutes and 2 minutes, respectively for the three overall mix stages.

[0114] After each mixing step the rubber mixture was batched off on a mill, mill mixed for a short period of time, and slabs of rubber removed from the mill and allowed to cool to a temperature of 30°C or lower.

[0115] The amount of the silane condensation promoter is listed as being "variable" in Table 1 and are more specifically set forth in Table 2.

Table 1

<u>1st Preparatory, Non-Productive, Mixing Stage</u>	
Elastomer ¹	100
Processing Oil	14
Antioxidant ²	10
Silica ³	83
Organosilane disulfide composite ⁴	13.3
Pentaethylenehexamine ⁵	variable
<u>Final, Productive, Mixing Stage</u>	
Sulfur	1.4
Accelerator, sulfenamide type	1.6
Zinc oxide	3
Fatty Acid	2

1) a combination of elastomers, namely, cis 1,4-polyisoprene natural rubber, E-SBR obtained from The Goodyear Tire & Rubber Company containing 40 percent styrene and having a Tg of -31°C, isoprene/butadiene (50/50) copolymer elastomers having a Tg of -44°C obtained from The Goodyear Tire & Rubber Company, and cis 1,4-polybutadiene elastomer obtained as BUDENB[®] 1207 from The Goodyear Tire & Rubber Company, in a dry rubber weight ratio of 10/25/45/20; with the E-SBR being oil extended so that it contains 25 phr rubber and 15 phr oil;

2) a phenylene diamine type;
 3) Zeosil 1165 MP from Rhone Poulenc;
 4) a composite commercially available from Degussa AG as X266S in a form of a 50/50 blend of a bis-(3-triethoxysilylpropyl) disulfide as the coupler, having an average of 2.2 sulfur groups in its polysulfidic bridge, with carbon black and, thus, the disulfide is considered as being 50% of the composite;
 5) Liquid pentaethylenehexamine, greater than 75 percent purity, as a silane condensation promoter from the Aldrich S.A. Company.

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Table 2

Material	Sample A Control	Sample B	Sample C
Pentaethylenehexamine	0	2	4
Physical Properties			
Mooney (ML4) P1	65	85	106
Insoluble polymer (%)	58	67	76
Rheometer (150°C)			
Max. Torque, MPa	41.1	37.8	40.5
Min. Torque, MPa	15.8	15.3	16.2
Delta Torque	25.3	22.5	24.3
T ₉₀ , minutes	9.2	10.5	11.0
Stress-Strain			
Tensile Strength, MPa	14.2	13.4	12.7
Elongation @ Break, %	416	382	361
100% Modulus, MPa	2.2	1.9	1.8
300% Modulus, MPa	10.4	10.2	9.8
300/100 modulus ratio	4.7	5.3	5.45
Rebound			
100°C, %	60.5	62	62
Hardness (Shore A)			
25°C	65	63	60
DIN Abrasion at 10 Newtons			
mm ³ volume loss	103	96	80

[0116] From Table 2 it can readily be seen that addition of the organosilane disulfide plus the controlled addition of the silane condensation promoter results in some improvement of silica/silica/polymer interactions and related rubber composition properties as is exemplified in Table 2 by increased insoluble polymer fraction, higher modulus ratio, and lower DIN abrasion volume loss.

[0117] For this Example, the insoluble polymer fraction is determined by gel permeation chromatography using tetrahydrofuran (THF) as a solvent for 24 hours. Such determination is understood to be well known to those having skill in such art.

[0118] This is considered as being advantageous because of an improved resistance to wear.

[0119] This Example further shows that the rubber composition's hysteresis is improved as silane condensation promoter is added as exemplified in Table 2 by an increase in its hot rebound values.

[0120] This is also considered herein as being advantageous because it should promote a reduction in a tire having a tread of such rubber composition and to thereby promote a reduction in vehicular fuel consumption.

50 EXAMPLE II

[0121] Sulfur-vulcanizable rubber compositions which contain silica reinforcement are prepared utilizing a relatively high purity bis(3-triethoxysilylpropyl) disulfide compound.

[0122] Such rubber compositions are identified herein as Samples D, E and F, with Sample D being considered herein as a Control sample.

[0123] For Samples E and F, a pentaethylenehexamine promoter is also added in the non-productive mixing stage after the silica-based filler and coupling agent have been added.

[0124] Rubber compositions containing the ingredients shown in Table 1 were prepared in a BR Banbury internal

rubber mixer via the aforesaid sequential three separate stages of mixing, namely, two preparatory mix stages followed by a final mix stage to temperatures of 170°C, 170°C and 120°C. The mixing time for the first preparation (non-productive) mixing step is variable and the mixing times for the second and third preparatory steps are two minutes each.

[0125] After each mixing step the rubber mixture was batched off on a mill, mill mixed for a short period of time, and 5 slabs of rubber removed from the mill and allowed to cool to a temperature of 30°C or lower.

Table 3

1st Preparatory, Non-Productive, Mixing Stage	
Elastomer ¹	100
Processing oil	14
Antioxidant ²	10
Silica ³	83
Organosilane disulfide composite ⁴	13.3
Pentaethylenehexamine ⁵	2
2nd preparatory, Non-Productive, Mixing Stage	
No additional ingredients added	
Final, Productive, Mixing Stage	
Sulfur	1.4
Accelerator, sulfenamide type	1.6
Zinc oxide	3
Fatty acid	2

30 1) a combination of elastomers, namely, cis 1,4-polyisoprene natural rubber, E-SBR obtained from The Goodyear Tire & Rubber Company containing 40 percent styrene and having a Tg of -31°C, isoprene/butadiene (50/50) copolymer elastomers having a Tg of -44°C obtained from The Goodyear Tire & Rubber Company, and cis 1,4-polybutadiene elastomer obtained as BUDENE® 1207 from The Goodyear Tire & Rubber Company, in a dry rubber weight ratio of 10/25/45/20; with the E-SBR being oil extended so that it contains 25 phr rubber and 15 phr oil;

35 2) a phenylene diamine type;

3) Zeosil 1165 MP from Rhone Poulenc;

4) a composite commercially available from Degussa AG as X266S in a form of a 50/50 blend of a bis-(3-triethoxysilylpropyl) disulfide coupling agent, having an average of 2.2 sulfur groups in its polysulfidic bridge, with carbon black and, thus, the disulfide is considered as being 50% of the composition; and

45 5) liquid pentaethylenehexamine, greater than 75 percent purity, as a silane condensation promoter from the Aldrich S.A. Company.

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Table 4

	<u>Sample D Control</u>	<u>Sample E</u>	<u>Sample F</u>	
5	1st preparatory stage	8	8	
10	mixing time, minutes		4	
15	<u>Material</u>			
20	Pantaethylanehexamina	0	2	
25	<u>Physical Properties</u>			
30	Mooney (ML4) P1	65	85	
35	Insoluble polymer (%)	58	67	
40	<u>Rheometer (150°C)</u>			
45	Max. Torque, MPa	41.9	37.8	
50	Min. Torque, MPa	15.8	15.3	
55	Delta Torque	25.3	22.5	
60	T ₉₀ , minutes	9.2	10.5	
65	<u>Stress-Strain</u>			
70	Tensile Strength, MPa	14.2	13.4	
75	Elongation @ Break, %	416	382	
80	100% Modulus, MPa	2.2	1.9	
85	300% Modulus, MPa	10.4	10.2	
90	300/100 modulus ratio	4.7	5.3	
95	<u>Rebound</u>			
100	100°C, %	60.5	62	
105	<u>Hardness (Shore A)</u>			
110	25°C	65	63	
115	<u>Din Abrasion at 10 Newtons</u>			
120	mm ³ volume loss	103	96	
125			105	

[0126] From Table 4 it can readily be seen that addition of the organosilane disulfide plus the controlled addition of the silane condensation promoter enabled the preparation of rubber composition F with physical properties substantially equal to those of Control Sample D while having the mixing time for the first preparatory mixing step reduced by a factor of two. This is seen as a very significant advantage in the processing of such a rubber composition.

Claims

1. A process of preparing a composite of an elastomer composition which contains a silica-based reinforcement therein characterized by comprising the sequential steps of:

(A) thermomechanically mixing in at least one preparatory mixing step to a temperature of 140°C to 190°C, (i) 100 parts by weight of at least one sulfur-vulcanizable elastomer selected from homopolymers and copolymers of conjugated diene hydrocarbons copolymers of at least one conjugated diene hydrocarbon and vinyl aromatic compound, (ii) 15 to 100 phr of particulate filler comprised of at least one silica-based filler which contains hydroxyl groups on the surface thereon, (iii) 0.05 to 20 parts by weight per part by weight of said particulate filler of at least one organosilane compound selected from at least one of Formula (I) and (II) their mixtures:

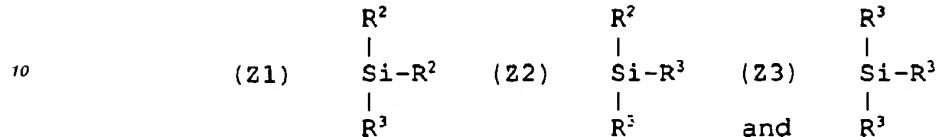
Z-R¹-Sn-R¹-Z

(I)

Z-R¹-X

(II)

5 wherein n is an integer of from 2 to 8 with an average of from 3.5 to 4.5, or an integer of from 2 to 4 with an average of from 2 to 2.6; wherein Z is selected from the group consisting of:



15 wherein R¹ is selected from the group consisting of a substituted or unsubstituted alkylene group having a total of 1 to 18 carbon atoms and a substituted or unsubstituted arylene group having a total of 6 to 12 carbon atoms; wherein R² may be the same or different and is individually selected from the group consisting of alkyls having 1 to 4 carbons and phenyl; and R³ may be the same or different and is individually selected from the group consisting of alkoxy groups having 1 to 4 carbon atoms, preferably from 1 to 2 carbon atoms; and wherein X is selected from mercapto, thiocyanato, amino, vinyl, epoxide, acrylate and methacrylate groups; (iv) subsequently mixing therewith at least one silane condensation reaction promoter and/or inhibitor; (B) subsequently blending sulfur therewith, in a final thermomechanical mixing step at a temperature from 100°C to 130°C.

25 2. The process of claim 1 characterized in that said silica-based filler is selected from at least one of precipitated silica, aluminosilicate and carbon black having silanol groups on the surface thereof; wherein said carbon black containing silanol groups on its surface is prepared by (a) treatment of carbon black with an alkoxy silane or (b) by co-fuming carbon black and silica.

30 3. The process of any of the preceding claims characterized in that said preparatory mixing is conducted in at least two sequential thermomechanical mixing steps in at least one internal rubber mixer; wherein at least two of said mixing steps are conducted to a temperature in a range of 140°C to 190°C, with intermediate cooling of the rubber composition between at least two of the said mixing steps to a temperature below 50°C; wherein said silane condensation reaction promoter and/or inhibitor is added subsequent to the addition of both of said particulate silica-based filler and organosilane polysulfide in the same or subsequent mixing stage; and wherein the polysulfidic bridge of said organosilane polysulfide contains an average of from 2 to 2.6 or from 3.5 to 4.5 sulfur atoms and is of the Formula (I) where Z is Z3, where R¹ is an unsubstituted alkylene group containing from 2 to 6 carbon atoms and R³ is selected from methyl and ethyl radicals.

40 4. The process of any of the preceding claims characterized in that said organo silane compound is selected from one or more of propyltriethoxy silane, methyltriethoxy silane, hexadecyltriethoxy silane and octadecyltriethoxy silane.

45 5. The process of any of the preceding claims characterized in that 5 to 40 phr of a starch composite comprised of starch and plasticizer is added in said preparatory mixing stage(s) (A); wherein said starch composite has a softening point in a range of 110°C to 160°C according to ASTM No. D1228; wherein said plasticizer contains hydroxyl groups on the surface thereon and comprises at least one of poly(ethylene vinyl acetate), cellulose acetate and diesters of dibasic organic acids having a softening point below 160°C.

50 6. The process of any of the preceding claims characterized in that said silane condensation promoter and/or inhibitor is selected from at least one of (a) basic promoters selected from ammonia, ammonium hydroxide, N-butylamine, terbutylamine, tetrahydrofuran (THF), sodium fluoride, various polyamines such as, for example, pentaethylene hexamine, diaminopropane, diethylenetriamine, triethylenetetramine, poly(allylaminehydrochloride), poly(L-lysine hydrobromide), poly(L-arginine hydrochloride) and poly(L-histidine hydrochloride), (b) acidic promoters selected from phosphoric acid, acetic acid, hydrofluoric acid and sulfuric acid, (c) metal salts selected from zinc sulfate, aluminum sulfate, zinc stearate, and aluminum stearate, (d) metal oxides selected from zinc oxide and aluminum oxide and (e) catalysts selected from bis(2-ethylhexanoate) tin, bis(neodecanoate) tin, and dibutyl tin diacetate, dibutyl tin dilaurate, stannous octoate, stannous acetate, lead naphthanate, cobalt naphthanate and zinc octoate.

7. The process of any of the preceding claims characterized in that, for said sulfur-vulcanizable elastomer, said conjugated dienes are selected from isoprene and 1,3-butadiene and said vinyl aromatic compounds are selected from styrene and alpha-methylstyrene; and wherein an organic solution polymerization derived elastomer selected from at least one of alkoxy terminated elastomer and tin coupled elastomer.
8. The process of claim 1 characterized in that the silica is a precipitated silica having a BET surface area in a range of 100 to 300 square meters per gram and a dibutylphthalate (DBP) value in a range of 150 to 350 cm³/100g (ASTM D2414), and a CTAB value in a range of 100 to 220 m²/g (ASTM D3849); and wherein said silica has a mercury porosimetry pore size distribution of: five percent or less of its pores with a diameter of less than 10 nm; 60 to 90 percent of its pores with a diameter of 10 to 100 nm; 10 to 30 percent of its pores with a diameter of 100 to 1000 nm and 5 to 20 percent of its pores with a diameter of greater than 1000 nm.
9. A rubber composition prepared by the process of any of the preceding claims.
10. A vulcanized rubber composition prepared by the process of any of the preceding claims 1 through 8 characterized in that said process comprises a subsequent step of sulfur vulcanizing the resulting rubber composition.
11. A tire characterized by having at least one component as the rubber composition of any of the preceding claims 9 or 10.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 11 2497

DOCUMENTS CONSIDERED TO BE RELEVANT							
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)				
X	EP 0 845 493 A (GOODYEAR TIRE & RUBBER) 3 June 1998 (1998-06-03) * abstract; claims; example 2 * * page 12, line 33 *	1-4,6-11	C08K5/548 C08J3/20 C08L21/00				
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A	MURAKAMI K ET AL: "SILICA AND SILANCE COUPLING AGENT FOR IN SITU REINFORCEMENT OF ACRYLONITRILE-BUTADIENE RUBBER" RUBBER CHEMISTRY AND TECHNOLOGY, US, RUBBER DIVISION ACS, AKRON, vol. 72, no. 1, 1999, pages 119-129, XP000874205 ISSN: 0035-9475 * abstract * * page 125, paragraph 2 *	1-11					
P,X	EP 1 002 835 A (GOODYEAR TIRE & RUBBER) 24 May 2000 (2000-05-24) * abstract; claims; example III.V *	1-11					
<table border="1"> <tr> <td colspan="2">TECHNICAL FIELDS SEARCHED (Int.Cl.7)</td> </tr> <tr> <td colspan="2">C08K C08L</td> </tr> </table>				TECHNICAL FIELDS SEARCHED (Int.Cl.7)		C08K C08L	
TECHNICAL FIELDS SEARCHED (Int.Cl.7)							
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<p>The present search report has been drawn up for all claims</p>							
Place of search	Date of completion of the search		Examiner				
THE HAGUE	28 August 2000		Mettler, R-M				
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons B : member of the same patent family, corresponding document					
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ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 00 11 2497

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-08-2000

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